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Intramolecular hydrogen bond controlled monodentate *S*-coordination of *N*-phosphoryl-*N*′-(R)-thioureas with Pd(II)

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Abstract

Reaction of *N*-phosphorylated thioureas RNHC(S)NHP(O)(O*i*Pr)$_2$ (R = *t*Bu, **HL^{I}**; R = Ph, **HL^{II}**; R = 4′-benzo-15-crown-5, **HL^{III}**) with Pd(PhCN)$_2$Cl$_2$ in acetonitrile leads to complexes of formulae Pd(HL^{I}-*S*)$_2$Cl$_2$ (**1**), Pd(HL^{II}-*S*)$_2$Cl$_2$ (**2**) and Pd(HL^{III}-*S*)$_2$Cl$_2$ (**3**). The crystal structure of complex **1** has been investigated by X-ray crystallography. It was established that the thiourea ligands are in a *trans*-configuration and the palladium(II) cation is coordinated by the sulfur atoms of the C=S groups and the chlorine atoms. Complex **1** is the first example of palladium(II) complex in which the potentially chelating *N*-phosphorylated thiourea ligand is bound through the sulfur atom only.

Keywords: Complex; Crown-ether; Monodentate coordination; Palladium(II); Thiourea

The coordination chemistry of polyfunctional ligands, capable to realize different coordination modes with metal cations [1], is of interest for the synthesis of new selective complexing agents and analytical reagents. Koch and others have shown that the coordination of *N*,*N*-dialkyl-*N*′-aroylthioureas leads to bidentate-*O*,*S*-coordination to Pd(II) [2,3]. It was also shown that the coordination mode of *N*-alkyl-*N*′-aroylthioureas depends on an intramolecular hydrogen bond between the donor oxygen atom of the carbonyl group and the hydrogen atom of the NH group [2].

We have become interested in the coordination chemistry of *N*-phosphorylated thioureas RR′NC(S)NHP(O)(O*i*Pr)$_2$ (R = R′ = alkyl; R = H, R′ = alkyl, aryl) towards various transition metal cations [4] in view of their application in metals separations [5]. Recently, we reported, that in the square-planar complexes of *N*-phosphorylthioureas M[RNHC(S)NP(O)(O*i*Pr)$_2$]$_2$, where M = Ni(II), R = Ph [6], *p*-MeOC$_6$H$_4$, *p*-BrC$_6$H$_4$, *t*Bu, *i*Pr, *c*-Hex [7]; M = Pd(II), R = Ph [6], *i*Pr [7]; M = Cu(II), R = Ph, *c*-Hex [6], 1,3-*N*,*S*-coordination of the anionic ligand is realized.

Herein, we report the comparative study on the complexes of the Pd(II) ions with *N*-phosphorylthioureas, containing secondary nitrogen at the *N*-thioacylamidophosphate moiety C(S)NHP(O)(O*i*Pr)$_2$ (Scheme 1). The crystal structure of *trans*-Pd(HL^{I}-*S*)$_2$Cl$_2$, the first example of *N*-phosphorylthiourea coordinated to Pd(II) only through the S atom in the monodentate fashion, is also reported.

N-Phosphorylated thioureas were prepared as previously described [8] and purified by recrystallization from dichloromethane–*n*-hexane mixtures.

Complexes **1**–**3** were prepared by the following procedure: Pd(PhCN)$_2$Cl$_2$ was dissolved in acetonitrile and added to a solution containing the corresponding ligand in the same solvent (Scheme 1) [9]. The compounds obtained are crystalline solids that are soluble in most polar solvents.

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